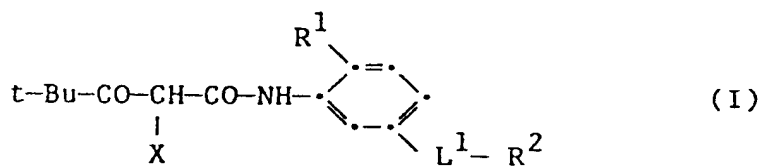




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(54) Title: PHOTOGRAPHIC SILVER HALIDE MATERIALS



## (57) Abstract

A photosensitive photographic colour material suitable for processing in a colour developer free of benzyl alcohol comprising a support bearing a silver halide emulsion, the halide content of which is at least 85 % chloride, which contains in or adjacent said silver halide layer: (1) a bisphenol derivative having two linked phenol rings, one of the phenolic hydroxy groups being substituted and at least one of the phenol rings being substituted, and (2) a ballasted yellow coupler of general formula (I), wherein L<sup>1</sup> is -NHSO<sub>2</sub>-, -SO<sub>2</sub>NH-, -OCO-, -COO-, -OSO<sub>2</sub>- or -SO<sub>2</sub>O-, R<sup>1</sup> is halogen or an alkyloxy group of 1-4 carbon atoms, R<sup>2</sup> is a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group of sufficient size and configuration to render the coupler non-diffusible in the photographic material, and X is a halogen, aryloxy, arylthio or heterocyclic coupling-off group.

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## PHOTOGRAPHIC SILVER HALIDE MATERIALS

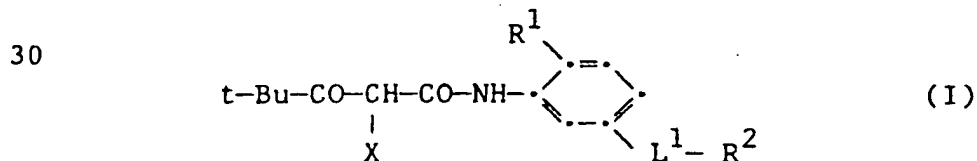
This invention relates to photographic silver halide materials.

5 European Patent Specification 0 246 766 (or US Patent 4 782 011) describes the stabilisation of photographic dye images using a bisphenol derivative having two linked phenol rings, one of the phenolic hydroxy groups being substituted and at least one of  
10 the phenol rings being substituted.

We have now found that the same bisphenol compounds will, in silver chloride emulsions suitable for processing in a colour developer free of benzyl alcohol, ensure that the performance of a certain  
15 class of yellow couplers is maximised.

According to the present invention therefore there is provided a photosensitive photographic colour material suitable for processing in a colour developer free of benzyl alcohol comprising a support bearing a  
20 silver halide emulsion, the halide content of which is at least 85% chloride, which contains in or adjacent said silver halide layer:

- (1) a bisphenol derivative having two linked phenol rings, one of the phenolic hydroxy groups being substituted and at least one of the phenol rings being substituted, and  
25 (2) a ballasted yellow coupler of the general formula:



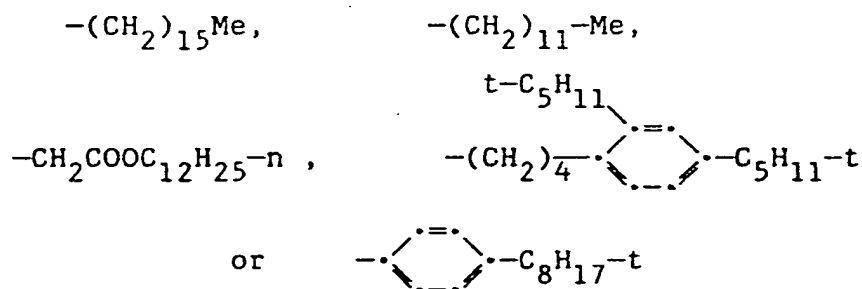
35 wherein  $\text{L}^1$  is  $-\text{NHSO}_2$ ,  $-\text{SO}_2\text{NH-}$ ,  $-\text{OCO-}$ ,  $-\text{COO-}$ ,  $-\text{OSO}_2\text{-}$  or  $-\text{SO}_2\text{O-}$ ,

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$R^1$  is halogen or an alkyloxy group of 1-4 carbon atoms,  
 $R^2$  is a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group  
 of sufficient size and configuration to render the coupler non-diffusible in the photographic material, and  
 X is a halogen, aryloxy, arylthio or heterocyclic coupling-off group.

The photographic materials of the present invention containing the combination of said stabilisers and said yellow image dye-forming couplers show maximised coupler performance as measured by higher  $D_{max}$  and/or gamma and reduced  $D_{min}$  of the dye image. Other known dye image stabilisers do not have this effect. Dye image stabilisation is also superior to that obtained with other known stabilisers.

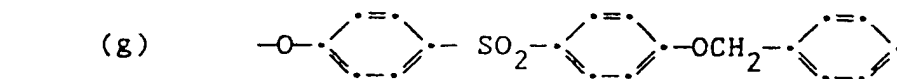
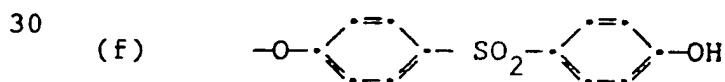
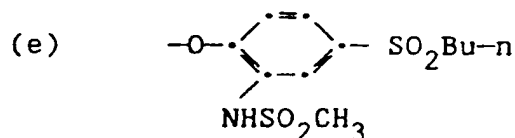
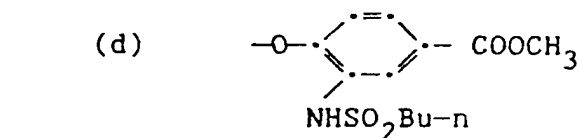
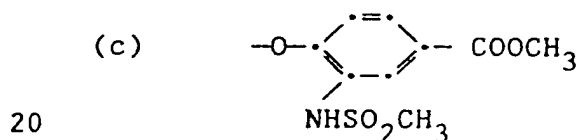
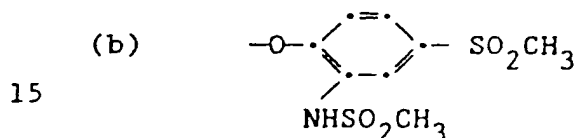
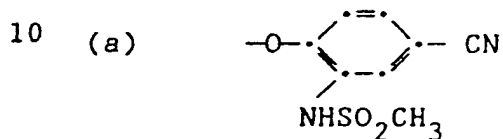
The ballasting groups  $R^2$  may include alkyl and/or aryl moieties optionally linked by ether or ester groups. Examples of such groups which may be employed are:

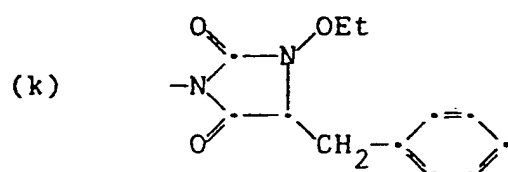
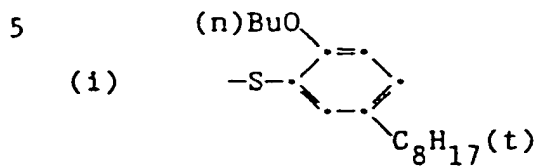
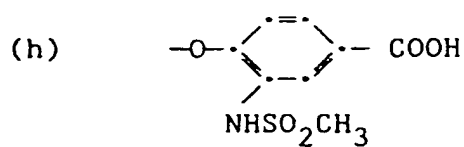


The coupling-off group X may be chlorine a heterocyclic group or an aryloxy or arylthio group optionally substituted with alkyl or arylsulphonyl, alkylsulphonamido, or alkoxycarbonyl groups which

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themselves are optionally substituted. Preferred coupling-off groups are phenoxy groups containing electron-withdrawing substituents at the ortho- and/or para positions, especially at the para- and one  
 5 ortho-position. In addition, ionisable substituents are also beneficial. Examples of coupling-off groups that may be used are the following:





15

Examples of couplers according to the present invention are listed in the following Table.

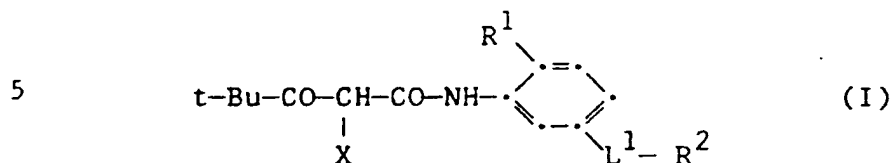
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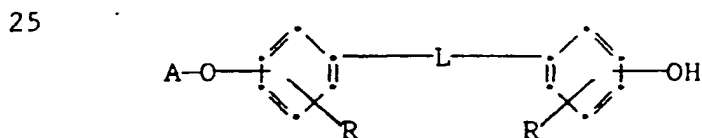
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TABLE 1



	Coupler	R <sup>1</sup>	R <sup>2</sup>	X	L <sup>1</sup>
10	1	Cl	-(CH <sub>2</sub> ) <sub>15</sub> Me	(f)	-NH <sub>2</sub> SO <sub>2</sub>
	2	CH <sub>3</sub> O-	-(CH <sub>2</sub> ) <sub>15</sub> Me	(c)	"
	3	Cl	-(CH <sub>2</sub> ) <sub>11</sub> Me	(g)	"
15	4	Cl	$\begin{array}{c} \text{t-C}_5\text{H}_{11} \\   \\ \text{---}(\text{CH}_2)_4\text{---} \end{array} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{---C}_5\text{H}_{11}\text{---t} \end{array}$	(f)	"
	5	Cl	C <sub>12</sub> H <sub>25</sub> -n	(k)	-CO-O-
	6	Cl	C <sub>16</sub> H <sub>33</sub> -n	(k)	-O-SO <sub>2</sub> -
20					

A preferred group of stabilisers is represented by the following general formula



wherein

30 A is a blocking group such as alkyl e.g. methyl, ethyl, propyl or butyl; cycloalkyl e.g. cyclohexyl; alkenyl; aryl e.g. phenyl; acyl e.g. acetyl or benzoyl; alkylsulphonyl or arylsulphonyl;

L is a single bond or a linking group such as  
35 alkylene e.g. methylene; alkylidene e.g. butylidene or

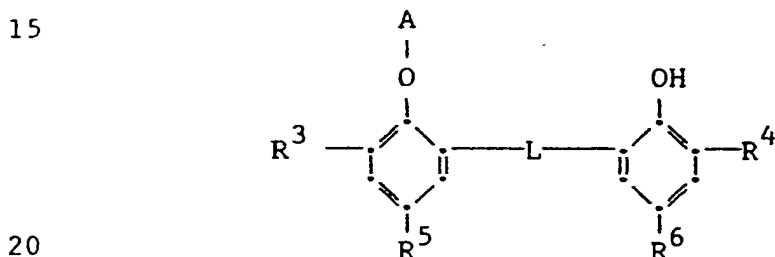
-6-

3,5,5,-trimethylhexylidene; a heteroatom e.g. oxygen or sulphur; or sulphonyl; and,

each R independently represents one or more substituents each independently selected from alkyl, alkoxy, alkenyl, cycloalkyl, or aryl; or each R independently represents the atoms necessary to complete with the benzene ring to which it is attached a fused polycyclic aromatic ring structure;

all the above mentioned alkyl, cycloalkyl, alkylene, alkenyl, acyl and aryl groups being optionally substituted.

Particularly preferred stabilizers are represented by the general formula



wherein

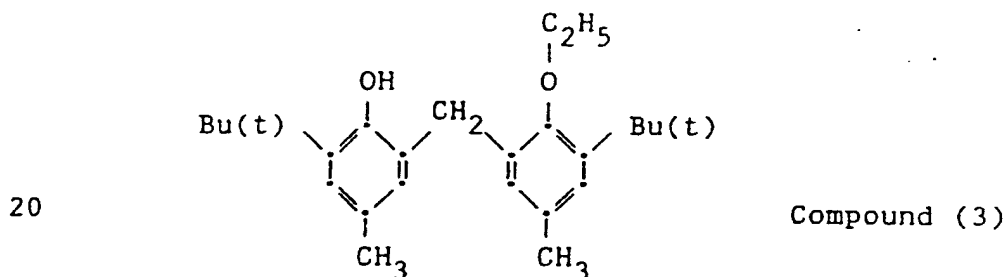
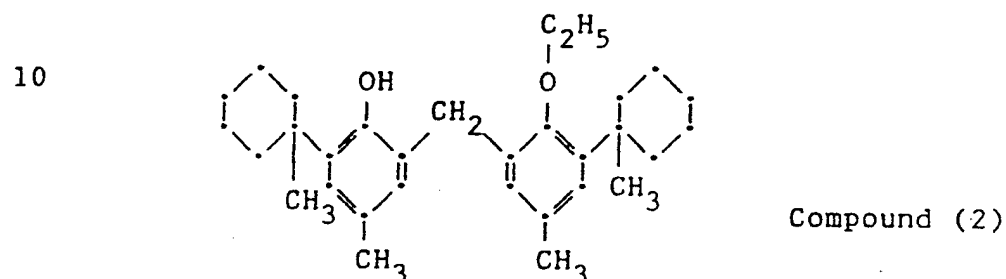
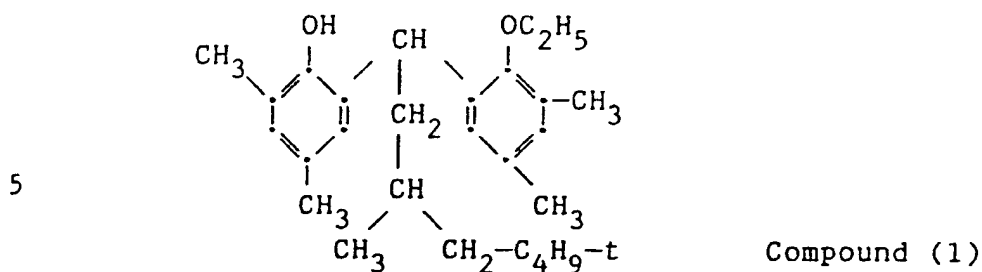
A and L are as defined above; and,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  each independently represent substituted or unsubstituted alkyl, alkenyl, cycloalkyl or aryl. Preferably,  $R^3$  and  $R^4$  are identical and  $R^5$  and  $R^6$  are identical.

Alkylidene bisphenols represent a preferred group of stabilizers in which the linking group L may be  $-(CR^7R^8)_n-$  wherein each of  $R^7$  and  $R^8$  independently is hydrogen or optionally substituted alkyl, cycloalkyl, alkenyl or aryl and n is an integer from 1 to 10, preferably 1 to 3, most preferably 1.

Specific examples of a stabilizer suitable for use in the present invention are as follows:



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Other examples are listed in European Specification  
0 246 766.

25 The silver halide preferably comprises at  
least 95% chloride and is preferably substantially  
pure silver chloride.

Typically both the coupler and the bisphenol  
30 derivative are dissolved in a coupler solvent and this  
solution is dispersed in an aqueous gelatin solution.  
Examples of coupler solvents that may be used are  
dibutyl phthalate, tricresyl phosphate, diethyl  
lauramide and 2,4-di-tertiary-amyphenol. In addition  
35 an auxiliary coupler solvent may also be used, for  
example ethyl

acetate, cyclohexanone, and 2-(2-butoxy-ethoxy)ethyl acetate, which are removed from the dispersion before incorporation into the photographic material.

5 The photographic elements can be single colour elements or multicolour elements. In a multicolour element, the yellow dye-forming couplers of this invention would usually be associated with a blue-sensitive emulsion, although they could be associated with an emulsion sensitised to a different  
10 region of the spectrum, or with a panchromatically sensitised, orthochromatically sensitised or unsensitised emulsion. Multicolour elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be  
15 comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the elements, including the layers of the image-forming units, can be arranged in various orders as known in the art.

20 A typical multicolour photographic element comprises a support bearing a yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler and magenta and  
25 cyan dye image-forming units comprising at least one green- or red-sensitive silver halide emulsion layer having associated therewith at least one magenta or cyan dye-forming coupler respectively. The element can contain additional layers, such as filter layers.

30 In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1978, Item 17643, published by Industrial Opportunities Ltd., The Old Harbourmaster's,  
35 8 North Street, Emsworth, Hants PO10 7DD, U.K. This

publication will be identified hereafter as "Research Disclosure".

The silver halide emulsion employed in the elements of this invention can be either  
5 negative-working or positive-working. Suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited therein. Suitable vehicles for the emulsion layers and other layers of elements of this  
10 invention are described in Research Disclosure Section IX and the publications cited therein.

In addition to the couplers of this invention, the elements of the invention can include additional couplers as described in Research  
15 Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. The couplers of this invention and any additional couplers can be incorporated in the elements and emulsions as described in Research Disclosures of Section VII,  
20 paragraph C and the publications cited therein.

The photographic elements of this invention or individual layers thereof, can contain brighteners (see Research Disclosure Section V), antifoggants and stabilisers (see Research Disclosure Section VI),  
25 antistain agents and image dye stabiliser (see Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (see Research Disclosure Section VIII), hardeners (see Research Disclosure Section XII, plasticisers and lubricants  
30 (see Research Disclosure Section XIII), matting agents (see Research Disclosure Section XVI) and development modifiers (see Research Disclosure Section XXI).

The photographic elements can be coated on a variety of supports as described in Research  
35 Disclosure Section XVII and the references described

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therein.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed to form a visible dye image as described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the elements with a colour developing agent to reduce developable silver halide and oxidise the colour developing agent. Oxidised colour developing agent in turn reacts with the coupler to yield a dye.

Preferred colour developing agents are p-phenylene diamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N- $\beta$ -(methanesulphonamido)-ethylaniline sulphate hydrate, 4-amino-3-methyl-N-ethyl-N- $\beta$ -(methanesulphonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulphonate.

With negative-working silver halide emulsions this processing step leads to a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromagenic developing agent to develop exposed silver halide, but not form dye, and then uniform fogging of the elements to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

The invention is illustrated by the following Examples.

35

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Example 1

Two dispersions of Coupler (1) in gelatin, with and without added Compound (1), were prepared by ultrasonic agitation (Dawe Instruments "Soniprobe").

5 Details of the method are given below:

(i) Oil Solution:

	Coupler (1)	3.28g
	dibutyl phthalate	0.82g
10	2-(2-butoxyethoxy)ethyl acetate	0.82g
	Compound (1)	1.64g

(ii) Gel Solution:

	12.5% aq. gelatin solution	36.0g
15	10% aq. diisopropylnaphthalene	
	sulphonic acid sodium salt	2.0ml

The components of the oil solution were heated together at 120°C to effect solution. A small quantity of ethyl acetate (0.5g) was added to help  
20 this process and this was evaporated off before continuing. The gelatin mixture, melted at 60°C, was added to the hot oil and the mixture agitated with the ultrasonic probe for 4 minutes and chilled.

A similar dispersion of a check Coupler (A)  
25 (identified below) without stabiliser was also prepared.

The Coupler (1) dispersions were coated with a blue-sensitive AgCl emulsion to give coatings of the following structure:

30

35

-12-

5	Layer 1	Gel	$1.610 \text{ g.m}^{-2}$
		BVSME*	$0.065 \text{ g.m}^{-2}$
10	Layer 2	Coupler (1)	$0.588 \text{ g.m}^{-2}$
		Compound(2)	$0.294 \text{ g.m}^{-2}$
		Ag	$0.267 \text{ g.m}^{-2}$
		Gel	$1.61 \text{ g.m}^{-2}$
/// R-C Paper Support ///			

15 \*BVSME = bis-vinylsulphonylmethyl ether

The Coupler (A) dispersion was coated similarly except that the coupler coverage was increased to 0.753g per square metre.

20 The coatings were wedge-exposed and developer using RA4 processing solutions. Sensitometric parameters were recorded and the sample strips were then faded for 10 days through a UV filter in front of a high intensity light source (Xenon Arc, 50 Klux).  
 25 The loss of dye density from an initial value of 1.0 was recorded. The results are shown in the table below:

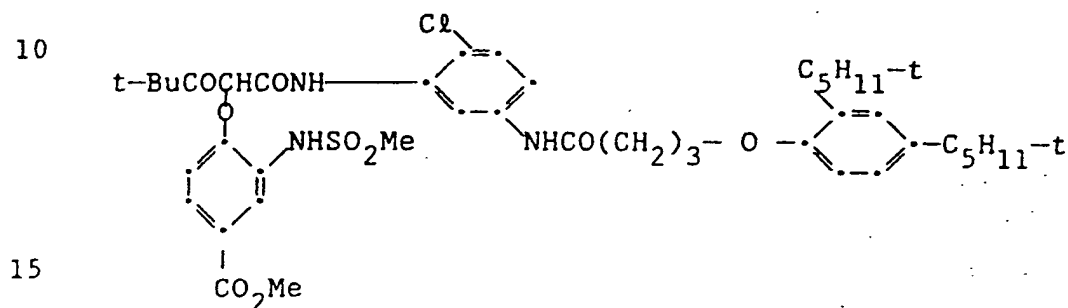
Coating	D(min)	D(max)	Gamma	Fade
30 Coupler (A)	0.08	1.81	2.95	-0.17
Coupler (1)	0.10	2.13	3.28	-0.60
Coupler (1) + Compound (1)	0.08	2.10	3.42	-0.12

35

-13-

The gamma, or contrast, values shown in the table can be taken to represent the photographic activity of the coatings. It is clear that the presence of Compound (1) improved the performance Coupler (1), and that both Coupler (1) coatings were superior to the Coupler (A) check, notwithstanding the 28% higher coverage of the check coupler.

Coupler (A) has the formula:



The recorded fades show that the presence of the stabiliser produces a substantial improvement in the light stability of the coupler (1) image dye, to the extent that it surpasses that of the (unstabilised) check.

#### Example 2

Further Coupler (1) dispersions were prepared and coated as in Example 1, containing, respectively, no stabiliser, and various stabilisers including some outside the present invention. Compared with Example 1, the coating coverages were reduced to 0.382g per square metre coupler and 0.17g per square metre Ag.

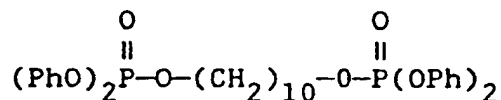
The coatings were evaluated in the same manner as in Example 1 and the Table below shows the results.

-14-

	Additive	D(min)	D(max)	Gamma	Fade*
	-	0.11	1.70	2.45	-0.59
	Compound (1)	0.09	1.73	2.71	-0.13
5	Compound (2)	0.09	1.70	2.60	-0.11
	Compound (A)	0.10	1.66	2.34	-0.37
	Compound (B)	0.09	1.32	2.17	-0.26

10 \* 7 days 50 klux fade, density loss from 1.0

The gamma values in the table confirm the sensitometric benefit of Compound (1) and show similar behaviour for its analogue, Compound (2). In contrast, both of  
 15 the comparison stabilisers,  
 Compound (A):



20 and Compound (B) (Irgaperm 1994 (trade of Ciba-Geigy)) were detrimental to sensitometry. Furthermore, these stabilisers were found to be significantly less effective than the two materials of this invention in reducing the fade of the image.

25

### Example 3

Coatings were made and tested as described in Example 1 using the couplers indicated below with silver and coupler coverages at  $0.465 \text{ g/m}^2$  and  
 30  $0.215 \text{ g/m}^2$  respectively. The results were as follows.

35



-15-

	Coating	D(min)	D(max)	Gamma	Fade
	Coupler (5)*	0.18	2.13	2.46	-0.61
5	Coupler (5) + Compound (1)	0.10	2.15	2.45	-0.11
	Coupler (6)**	0.23	1.71	2.30	-0.81
	Coupler (6) + Compound (1)	0.18	1.78	2.52	-0.49
10					

\* 7 days 50 klux fade, density loss from 1.0

\*\* 21 days 50 klux fade, density loss from 1.0

15 Improvements are seen in not only in fade results but both  $D_{min}$ ,  $D_{max}$  and, for Coupler (6), gamma as well.

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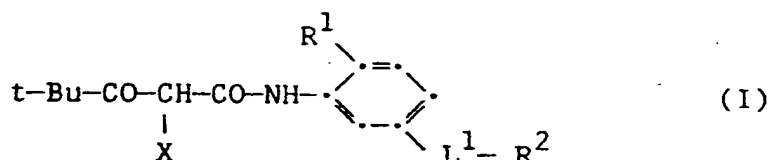
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## CLAIMS

1. A photosensitive photographic colour material suitable for processing in a colour developer free of benzyl alcohol comprising a support bearing a silver halide emulsion, the halide content of which is at least 85% chloride, which contains in or adjacent said silver halide layer:

(1) a bisphenol derivative having two linked phenol rings, one of the phenolic hydroxy groups being substituted and at least one of the phenol rings being substituted, and

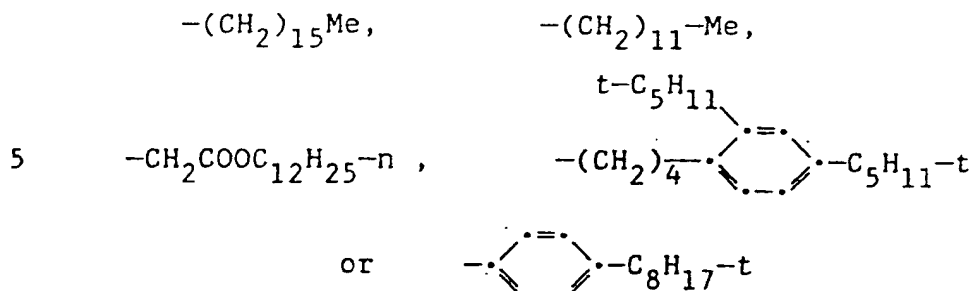
(2) a ballasted yellow coupler of the general formula:



wherein  $\text{L}^1$  is  $-\text{NHSO}_2$ ,  $-\text{SO}_2\text{NH}-$ ,  $-\text{OCO}-$ ,  $-\text{COO}-$ ,  $-\text{OSO}_2-$  or  $-\text{SO}_2\text{O}-$ ,  
 $\text{R}^1$  is halogen or an alkyloxy group of 1-4 carbon atoms,  
 $\text{R}^2$  is a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group of sufficient size and configuration to render the coupler non-diffusible in the photographic material, and  
 $\text{X}$  is a halogen, aryloxy, arylthio or heterocyclic coupling-off group.

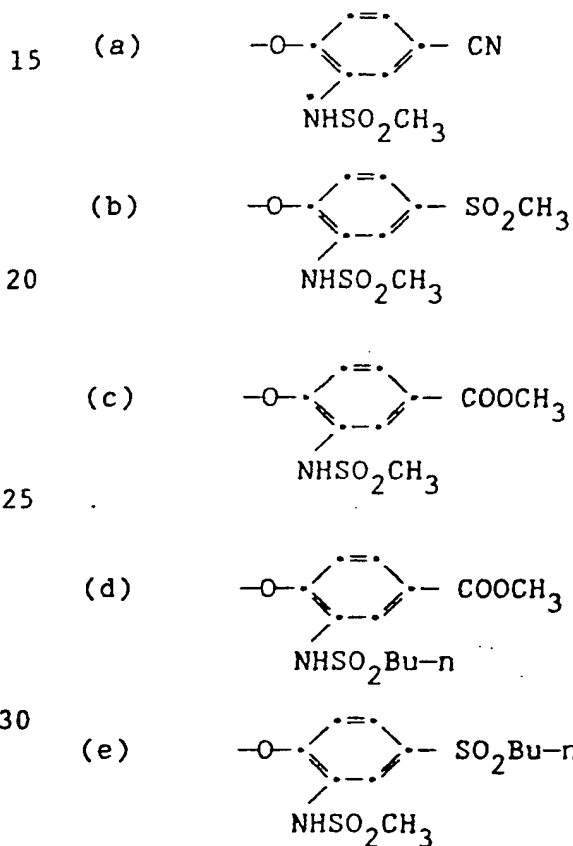
2. A photographic material as claimed in claim 1 wherein the group  $\text{R}^2$  comprises a group:

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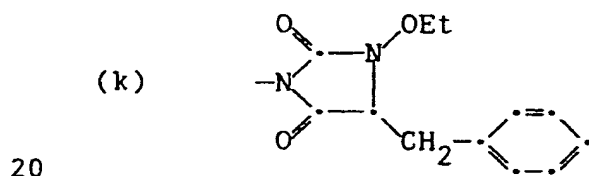
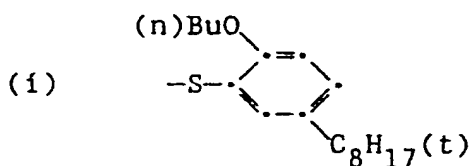
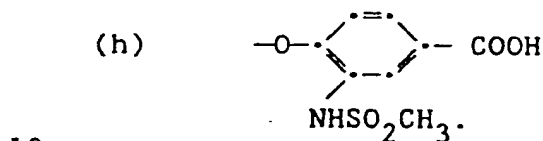
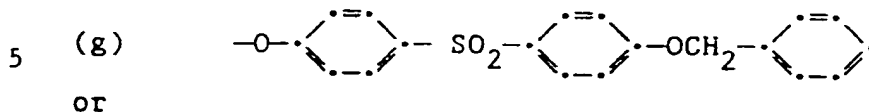
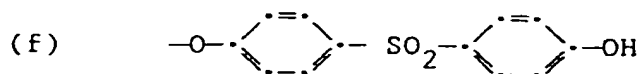
3. A photographic material as claimed in claim 1  
 10 or 2 in which the group  $R^1$  is chloro or methoxy.

4. A photographic material as claimed in any of  
 claims 1-3 in which the coupling off group X is one of  
 the following:

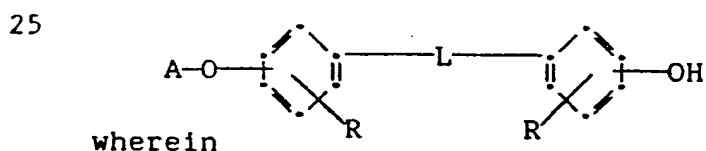


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-18-



5. A photographic material as claimed in any of claims 1-4 in which the bisphenol derivative has the general formula:



A is a blocking group such as alkyl e.g. methyl, ethyl, propyl or butyl; cycloalkyl e.g. cyclohexyl; alkenyl; aryl e.g. phenyl; acyl e.g. acetyl or benzoyl; alkylsulphonyl or arylsulphonyl;

30

L is a single bond or a linking group such as alkylene e.g. methylene; alkylidene e.g. butylidene or 3,5,5-trimethylhexylidene; a heteroatom e.g. oxygen

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-19-

or sulphur; or sulphonyl; and,

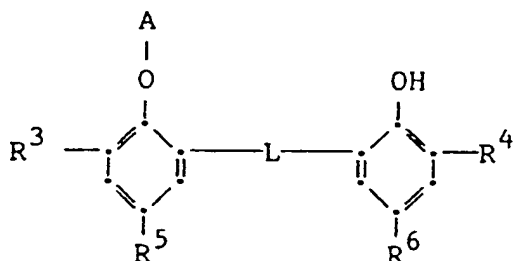
each R independently represents one or more substituents each independently selected from alkyl, alkoxy, alkenyl, cycloalkyl, or aryl; or each R

5 independently represents the atoms necessary to complete with the benzene ring to which it is attached a fused polycyclic aromatic ring structure;

all the above mentioned alkyl, cycloalkyl, alkylene, alkenyl, acyl and aryl groups being  
10 optionally substituted.

6. A photographic material as claimed in any of claims 1-5 in which the bisphenol derivative has the general formula:

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wherein

A and L are as defined above; and,

$\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  each independently

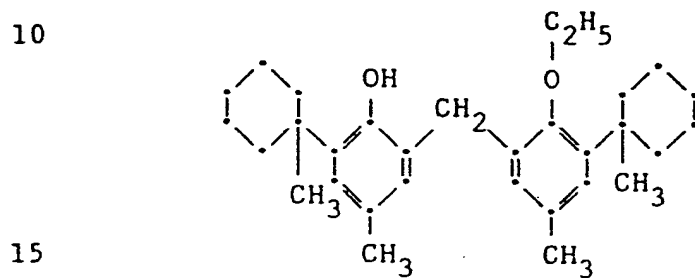
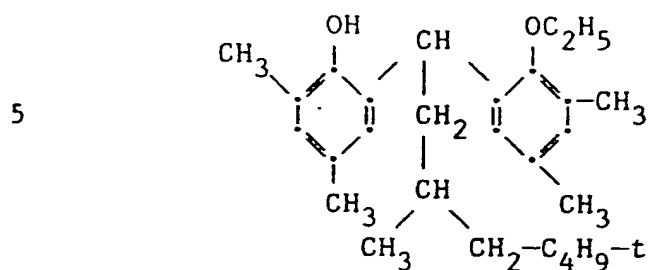
25 represents substituted or unsubstituted alkyl, alkenyl, cycloalkyl or aryl. Preferably,  $\text{R}^3$  and  $\text{R}^4$  are identical and  $\text{R}^5$  and  $\text{R}^6$  are identical.

Alkylidene bisphenols represent a preferred group of stabilizers in which the linking group L may  
30 be  $-(\text{CR}^7\text{R}^8)_n-$  wherein each of  $\text{R}^7$  and  $\text{R}^8$  independently is hydrogen or optionally substituted alkyl, cycloalkyl, alkenyl or aryl and n is an integer from 1 to 10, preferably 1 to 3, most preferably 1.

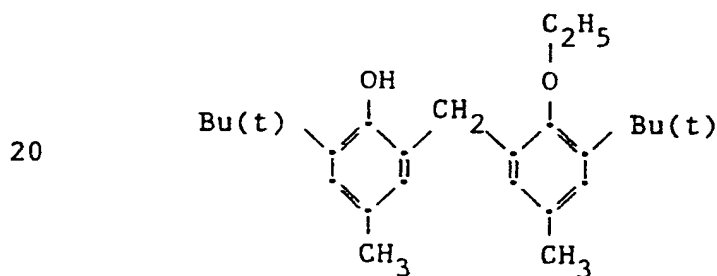
7. A photographic material as claimed in any of  
35 claims 1-6 in which the bisphenol compound has one of

-20-

the formulae:



and

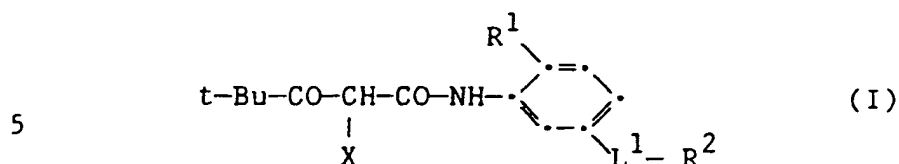


8. A photographic material as claimed in any of  
 25 claims 1-7 in which the coupler is one of those listed  
 in the following Table:

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	Coupler	R <sup>1</sup>	R <sup>2</sup>	X	L <sup>1</sup>
10	1	Cl	-(CH <sub>2</sub> ) <sub>15</sub> Me	(f)	-NH <sub>2</sub> SO <sub>2</sub>
	2	CH <sub>3</sub> O-	-(CH <sub>2</sub> ) <sub>15</sub> Me	(c)	"
	3	Cl	-(CH <sub>2</sub> ) <sub>11</sub> Me	(g)	"
15	4	Cl	$  \begin{array}{c}  \text{t-C}_5\text{H}_{11} \\  \diagup \quad \diagdown \\  \text{C} = \text{C} \\  \diagdown \quad \diagup \\  \text{C}_5\text{H}_{11}\text{-t}  \end{array}  $	(f)	"
	5	Cl	C <sub>12</sub> H <sub>25</sub> -n	(k)	-CO-O-
	6	Cl	C <sub>16</sub> H <sub>33</sub> -n	(k)	-O-SO <sub>2</sub> -

- 20 9. A photographic photosensitive material comprising a support bearing a layer of a photosensitive silver halide emulsion and, associated therewith a coupler and a blocked bis-phenol as defined in any of claims 1 - 8.
- 25 10. A multicolour photographic element comprising a support bearing a yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one coupler and one blocked bis-phenol as defined in
- 30 any of claims 1 - 8 and magenta and cyan dye image-forming units comprising at least one green- or red-sensitive silver halide emulsion layer having associated therewith at least one magenta or cyan dye-forming coupler respectively.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 90/01963

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: G 03 C 7/36, 1/34 // C 07 C 39/16														
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">G 03 C</td> </tr> </table> <div style="text-align: center; margin-top: 10px;"> <small>Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></small> </div>			Classification System	Classification Symbols	IPC5	G 03 C								
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IPC5	G 03 C													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category<sup>*</sup></th> <th style="width: 60%;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 30%;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>           US, A, 4782011 (JOHN D. GODDARD ET AL)            1 November 1988, see column 2,            line 14; column 3, line 13;            column 5, line 40 - line 50;            column 7, line 10 - line 20            column 7, line 66  <div style="text-align: center;">--</div> </td> <td style="text-align: center; vertical-align: top;">1-7,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>           US, A, 3933501 (ROBERT G. CAMERON ET AL)            20 January 1976, see column 11,            line 10 - line 20; column 14,            line 60 - line 65  <div style="text-align: center;">--</div> </td> <td style="text-align: center; vertical-align: top;">1-7,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>           US, A, 4783397 (AKIRA OGAWA ET AL)            8 November 1988, see column 17,            line 55 - line 65  <div style="text-align: center;">--</div> </td> <td style="text-align: center; vertical-align: top;">1-7,9</td> </tr> </tbody> </table>			Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	US, A, 4782011 (JOHN D. GODDARD ET AL) 1 November 1988, see column 2, line 14; column 3, line 13; column 5, line 40 - line 50; column 7, line 10 - line 20 column 7, line 66 <div style="text-align: center;">--</div>	1-7,9	Y	US, A, 3933501 (ROBERT G. CAMERON ET AL) 20 January 1976, see column 11, line 10 - line 20; column 14, line 60 - line 65 <div style="text-align: center;">--</div>	1-7,9	Y	US, A, 4783397 (AKIRA OGAWA ET AL) 8 November 1988, see column 17, line 55 - line 65 <div style="text-align: center;">--</div>	1-7,9
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:<sup>10</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">           Date of the Actual Completion of the International Search  <div style="border: 1px solid black; padding: 5px; text-align: center;">8th February 1991</div> </td> <td style="width: 50%; border: none;">           Date of Mailing of this International Search Report  <div style="border: 1px solid black; padding: 5px; text-align: center;">28.02.91</div> </td> </tr> <tr> <td style="border: none;">           International Searching Authority  <div style="border: 1px solid black; padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none;">           Signature of Authorized Officer  <div style="display: flex; align-items: center;"> <div style="flex: 1;">miss T. MORTENSEN</div> <div style="flex: 1; text-align: right;"> </div> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="border: 1px solid black; padding: 5px; text-align: center;">8th February 1991</div>	Date of Mailing of this International Search Report <div style="border: 1px solid black; padding: 5px; text-align: center;">28.02.91</div>	International Searching Authority <div style="border: 1px solid black; padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="flex: 1;">miss T. MORTENSEN</div> <div style="flex: 1; text-align: right;"> </div> </div>								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	EP, A2, 0231832 (FUJI PHOTO FILM CO., LTD.) 12 August 1987, see page 61  --	1-7,9
Y	EP, A2, 0256531 (FUJI PHOTO FILM CO., LTD.) 24 February 1988, see page 66  --	1
Y	EP, A2, 0230659 (FUJI PHOTO FILM CO., LTD.) 5 August 1987, see page 64  --  -----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 90/01963

SA 41628

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The members are as contained in the European Patent Office EDP file on 28/12/90  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4782011	01/11/88	EP-A- 0246766 JP-A- 62262047	25/11/87 14/11/87
US-A- 3933501	20/01/76	BE-A- 822726 CA-A- 1025473 CA-B- 1053698 CH-A- 589310 DE-A-B-C 2456076 FR-A-B- 2252591 GB-A- 1474128 JP-A- 50087650 JP-B- 57053944 US-E- RE30211	28/05/75 31/01/78 01/05/79 30/06/77 24/07/75 20/06/75 18/05/77 14/07/75 16/11/82 12/02/80
US-A- 4783397	08/11/88	JP-A- 62153954	08/07/87
EP-A2- 0231832	12/08/87	EP-A- 0234292 JP-A- 63011939 US-A- 4840878	02/09/87 19/01/88 20/06/89
EP-A2- 0256531	24/02/88	JP-A- 63044658 US-A- 4946770	25/02/88 07/08/90
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